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(US). SAMUELS, Sam, L. [US/US]; 34 Pelham Drive,
Landenberg, PA 19350 (US). SIEMIONKO, Roger, K.
[US/US]; 14107 Dorsetshire Court, Midlothian, VA 23113
(US).

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(74) Agent: DOBSON, Kevin, S.; E.I. Dupont De Nemours
and Company, Legal Patent Records Center, 4417 Lan-
caster Pike, WILMINGTON, DE 19805 (US).

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(71) Applicant (*for all designated States except US*): E.I. DU
PONT DE NEMOURS AND COMPANY [US/US]; 1007
Market Street, Wilmington, DE 19898 (US).

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(72) Inventors; and

(75) Inventors/Applicants (*for US only*): CHOU, Richard,
T. [US/US]; 173 Thompson Drive, Hockessin, DE 19707

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(54) Title: FLUORINE-CONTAINING ETHYLENE COPOLYMERS

(57) Abstract: The present invention is a fluorine containing ethylene copolymer (FCEC) obtained by the copolymerization of ethylene with suitable fluorine-containing comonomer compounds, wherein the fluorine-containing comonomer compound is present at a concentration of up to 40% by weight, based on the total weight of the ethylene copolymer. FCEC described herein can be useful in a variety of applications, for example: as a release resin in low surface energy release films; as melt blown fibers; in composite or multilayer structures as a low surface energy outer layer; as microporous membranes; as flashspun plexifilamentary products; and as melt spun fibrous products.

TITLE**FLUORINE-CONTAINING ETHYLENE COPOLYMERS**

This application claims the benefit of U.S.
5 Provisional Application No. 60/362,703, filed March 7,
2002.

BACKGROUND OF THE INVENTION**Field of the Invention**

The present invention relates to ethylene
10 copolymers. This invention particularly relates to
fluorine-containing ethylene copolymers and products
made therefrom.

Description of the Related Art

Fluoropolymer compositions are widely used for
15 surface modification, as agents to impart desirable
surface properties to various types of surfaces. For
example, fluoropolymer compositions can impart or
enhance the water and oil repellency of certain
surfaces, including fabrics and upholstery. However,
20 surface treatment using fluoropolymers can involve
complex processing steps to ensure that the
fluoropolymer is applied and bonded to the surface
being treated. The process can be difficult and
expensive. Organic solvent vapors can be released to
25 the atmosphere during the processing. Surface
treatment can involve high temperature curing of the
fluoropolymer to the substrate surface.

To impart water and oil repellency,
fluorochemicals or fluoropolymers can be dissolved or
30 dispersed either in organic solvents or in water. For
example, mixtures of fluorinated copolymers, mainly
comprising perfluoroalkyl methacrylate, and vinyl

copolymers are disclosed in U.S. Pat. No. 3,277,039.
U.S. Pat. No. 2,803,615 discloses acrylate/methacrylate
esters of N-alkyl or N-alkanol
perfluoroalkanesulfonamides used to impart grease and
5 oil repellency. Fluorochemical compositions for
treating textile fibers and fabrics comprising an
aqueous solution or dispersion of a fluorochemical
acrylate and a polyalkoxylated polyurethane having
pendant perfluoroalkyl groups is described in U.S. Pat.
10 No. 5,350,557. U.S. Pat. No. 5,536,304 describes a
composition for imparting water and oil repellency
comprising a fluoroaliphatic radical containing agent,
and a cyclic carboxylic acid anhydride-containing
polysiloxane.

15 Fluorochemicals can be melt-blended with
thermoplastic polymers, and thereby impart water and
oil repellency to the polymer by migrating to the
polymer surface as described in, for example, U.S. Pat.
No. 5,025,052, wherein the preparation of
20 fluoroaliphatic radical-containing oxazolidinone
compositions for blending with thermoplastic polymers
is described. U.S. Pat. No. 5,380,778 describes
thermoplastic compositions comprising fluoroaliphatic
radical containing aminoalcohols and a thermoplastic
25 synthetic organic polymer.

Ethylene copolymers are useful polymeric materials
in many applications. Ethylene copolymers can find use
in applications such as packaging, laminate films, and
adhesives for example. Conventional polyolefins such
30 as polypropylene, polyethylene, and conventional
ethylene copolymers have high surface tension relative
to fluoropolymers such as polytetrafluoroethylene, for

example. As a result, for applications wherein water and oil repellency is important, articles made from polyolefins must be treated to attain a satisfactory level of repellency. However, due to their relatively
5 low melting point and lack of reactive functional groups, treatment of polyolefins with fluorochemicals or fluoropolymers is, in general, much more difficult than treating other thermoplastic polymers.

Copolymers of ethylene and fluorine-containing
10 monomers are known. For example, Tefzel®, manufactured by E.I. DuPont de Nemours and Company, is a copolymer of ethylene and tetrafluoroethylene. Copolymers of this type are very different from conventional polyethylene copolymers in many aspects. For example,
15 fluorine-containing ethylene copolymers are typically melt-processable only at much higher temperature than conventional ethylene polymers and ethylene copolymers, and the properties of fluorine-containing ethylene copolymers differ from conventional ethylene
20 copolymers. Copolymers of this type are not amenable to manufacture or processing under the type of conditions used to manufacture and process conventional ethylene copolymers. Ethylene/fluoromonomer copolymers of this type are not compatible in systems that
25 currently use polyethylene copolymers. For example, known conventional ethylene/tetrafluoroethylene copolymers have no adhesion to polyethylene.

It would be desirable to have a fluorine-containing ethylene copolymer that can be processed in
30 the same way as conventional ethylene copolymers.

It would be desirable to have a melt-processable fluorine-containing ethylene copolymer.

It would be desirable to have a fluorine-containing ethylene copolymer that has a low surface tension.

It would be desirable to have a fluorine-
5 containing ethylene copolymer that can be compatible with, or used in place of conventional ethylene copolymers.

It would be desirable to have a laminate film having at least one layer of a fluorine-containing
10 ethylene copolymer.

It would be desirable to have at least a composite fiber having at least one component of a fluorine-containing ethylene copolymer.

SUMMARY OF THE INVENTION

15 In one aspect the present invention is a film comprising a fluorine containing ethylene copolymer (FCEC) obtained by the copolymerization of ethylene with suitable fluorine-containing comonomer compounds, wherein the FCEC comprises from about 0.5 wt% to about
20 40 wt% of a fluorine-containing comonomer compound and from about 30 wt% to about 99.5 wt% ethylene.

In another aspect the present invention is a fiber comprising a fluorine containing ethylene copolymer (FCEC) obtained by the copolymerization of ethylene
25 with suitable fluorine-containing comonomer compounds, wherein the FCEC comprises from about 0.5 wt% to about 40 wt% of a fluorine-containing comonomer compound and from about 30 wt% to about 99.5 wt% ethylene wherein the fiber is obtained by a melt-blowing process.

30 In another aspect the present invention is an article having a composite or multilayer structure comprising an outer layer comprising: a fluorine

containing ethylene copolymer (FCEC) obtained by the copolymerization of ethylene with suitable fluorine-containing comonomer compounds, wherein the FCEC comprises from about 0.5 wt% to about 40 wt% of a
5 fluorine-containing comonomer compound and from about 30 wt% to about 99.5 wt% ethylene.

In another aspect, the present invention is a microprobes membrane comprising a fluorine containing ethylene copolymer (FCEC) obtained by the
10 copolymerization of ethylene with suitable fluorine-containing comonomer compounds, wherein the FCEC comprises from about 0.5 wt% to about 40 wt% of a fluorine-containing comonomer compound and from about 30 wt% to about 99.5 wt% ethylene, wherein the membrane
15 is useful as protection against permeation of liquids through the membrane.

In still another aspect, the present invention is a flash spun plexifilamentary product comprising a fluorine containing ethylene copolymer (FCEC) obtained
20 by the copolymerization of ethylene with suitable fluorine-containing comonomer compounds, wherein the FCEC comprises from about 0.5 wt% to about 40 wt% of a fluorine-containing comonomer compound and from about 30 wt% to about 99.5 wt% ethylene.

25 In yet another aspect, the present invention is a melt spun fibrous article comprising a fluorine containing ethylene copolymer (FCEC) obtained by the copolymerization of ethylene with suitable fluorine-containing comonomer compounds, wherein the FCEC
30 comprises from about 0.5 wt% to about 40 wt% of a fluorine-containing comonomer compound and from about 30 wt% to about 99.5 wt% ethylene, wherein the fibrous

products are obtained by melt spinning or multicomponent fiber spinning a FCEC or a blend thereof.

DETAILED DESCRIPTION OF THE INVENTION

5 FCE copolymers of the present invention can be useful in a variety of applications. For example, copolymers of the present invention can be used: as a release resin in low surface energy release films; as melt blown fibers; in composite or multilayer
10 structures as a low surface energy outer layer; as microporous membranes; as flashspun plexifilamentary products; and as melt spun fibrous products.

In one embodiment, the present invention is an article comprising a fluorine-containing ethylene
15 copolymer (FCEC). Ethylene copolymers of the present invention include up to about 40% by weight, based on the total weight of the copolymer (wt%), of a suitable fluorine-containing monomer. Preferably the fluorine-containing comonomer is from about 2 to about 30 wt% of
20 the copolymer. More preferably, the fluorine-containing comonomer is from about 10 to about 25 wt% of the copolymer.

The copolymer comprises from about 30 wt% to about 99.5 wt% ethylene comonomer. Preferably the copolymer
25 comprises from about 40 wt% to about 95 wt% ethylene comonomer, more preferably from about 50 wt% to about 90 wt% ethylene comonomer, and most preferably from about 70 wt% to about 90 wt% ethylene comonomer.

The copolymer can optionally comprise other
30 comonomers. A copolymer, as the term is used herein, is a polymer obtained by the polymerization of at least two comonomers. A comonomer, as the term is used

herein, is any monomer that is polymerized in the presence of at least one other monomer to produce a copolymer of the present invention. For example, a copolymer can be the product of polymerization of two, three, four, or five comonomers, or more. Where the concentration of all but one of the comonomers is specified, the concentration of the remaining comonomer can be deduced by subtraction of the known constituents from 100 wt%, that is, the total wt% of the copolymer.

Suitable fluorine containing comonomers are described in U.S. Pat. No. 2,803,615; U.S. Pat. No. 2,642,416; US. Pat. No. 2,826,564; U.S. Pat. No. 3,102,103; US. Pat. No. 3,282,905; and US. Pat. No. 3,304,278, for example. Suitable fluorine-containing comonomers are fluorinated acrylate or methacrylate esters of the general formula: Cf-L-O-CO-CR=CH_2 , wherein:

(i) Cf is a fluorinated aliphatic group having at least 4 carbon atoms wherein the aliphatic group can be: straight chain or branched; acyclic or cyclic; and can include heteroatoms such as nitrogen, oxygen, and/or sulfur. It is preferable that Cf is a perfluorinated aliphatic group of the formula $\text{C}_n\text{F}_{2n+1}$, wherein n is an integer from 3 to 20;

(ii) L is a linking group that connects the fluorinated aliphatic group with the (meth)acrylate group, wherein L can contain from 1 to 10 carbon atoms, and can optionally include oxygen, nitrogen, or sulfur-containing groups, or combinations thereof; L can be straight-chain or branched, cyclic alkylene, arylene, arylalkylene,

sulfonyl, sulfoxy, sulfonamide, carboxyamino, carbonyloxy, urethanylene, or combinations thereof.

For example, a fluorine-containing monomer
 5 suitable for use in the present invention can include:

- $$\begin{aligned} & \text{CF}_3 - (\text{CF}_2)_n - \text{CH}_2 - \text{CH}_2 - \text{O} - \text{CO} - \text{CH} = \text{CH}_2; \\ & \text{CF}_3 - (\text{CF}_2)_n - \text{CH}_2 - \text{CH}_2 - \text{O} - \text{CO} - \text{C}(\text{CH}_3) = \text{CH}_2; \\ & \text{CF}_3 - (\text{CF}_2)_3 - \text{CH}_2 - \text{O} - \text{CO} - \text{CH} = \text{CH}_2; \\ & \text{CF}_3 - (\text{CF}_2)_3 - \text{CH}_2 - \text{O} - \text{CO} - \text{C}(\text{CH}_3) = \text{CH}_2; \\ 10 & \text{CF}_3 - (\text{CF}_2)_5 - \text{CH}_2 - \text{O} - \text{CO} - \text{CH} = \text{CH}_2; \\ & (\text{CF}_3)_2 - \text{CF} - (\text{CF}_2)_5 - \text{CH}_2\text{CH}_2 - \text{O} - \text{CO} - \text{CH} = \text{CH}_2; \\ & \text{CF}_3 - (\text{CF}_2)_7 - \text{SO}_2\text{N}(\text{CH}_3) - \text{CH}_2 - \text{CH}_2 - \text{O} - \text{CO} - \text{CH} = \text{CH}_2; \\ & \text{CF}_3 - (\text{CF}_2)_7 - \text{SO}_2\text{N}(\text{CH}_2\text{CH}_3) - \text{CH}_2 - \text{CH}(\text{CH}_3) - \text{O} - \text{CO} - \\ & \text{CH} = \text{CH}_2; \\ 15 & \text{CF}_3 - (\text{CF}_2)_5 - \text{SO}_2\text{N}(\text{CH}_3) - \text{CH}_2 - \text{CH}_2 - \text{O} - \text{CO} - \text{CH} = \text{CH}_2; \text{ and} \\ & (\text{CF}_3)_2 - \text{CF}(\text{CF}_2)_4 - \text{SO}_2\text{N}(\text{CH}_3) - \text{CH}_2 - \text{CH}_2 - \text{O} - \text{CO} - \text{CH} = \text{CH}_2, \end{aligned}$$

wherein n is an integer from 3 to about 20. Mixtures or physical combinations of comonomers described by the general formulas above are contemplated to be within
 20 the scope of the present invention. Furthermore, non-acrylic fluoroalkyl monomers can be used in the practice of the present invention, particularly when using transition metal catalysts.

Copolymers of the present invention can be
 25 prepared by conventional methods for polymerization or copolymerization of polyethylene polymers and copolymers. For example, copolymers of the present invention can be prepared by copolymerization of ethylene with fluorine containing comonomers described
 30 herein by high pressure free radical polymerization or, alternatively, by using low pressure transition metal catalysis. Using high pressure free radical

polymerization is preferred herein. Conventional methods for preparing ethylene copolymers are described in patented literature and reference textbooks. For example, an ethylene copolymerization process is
5 described in U.S. Pat. No. 4,351,931.

Copolymers of the present invention are melt-processable polymers and can be processed by methods used with conventional ethylene copolymers. For example, copolymers of the present invention can be
10 molded, extruded, blown, or spun to yield molded parts, fibers, or films, for example, in the same manner as conventional polyethylene polymers and copolymers.

Unlike conventional ethylene copolymers, polymers of the present invention have low surface tension.
15 Copolymers and copolymer blends of the present invention have surface tensions of less than those of conventional polyethylene and/or polypropylene polymers and copolymers. Copolymers (including blends) of the present invention have surface tensions of less than
20 about 32 dyne/cm. Preferably, the surface tension is less than about 28 dyne/cm, and more preferably less than about 24 dyne/cm.

In another embodiment, the present invention is a terpolymer comprising in addition to the above
25 comonomers, from about 0.5 wt% to about 5 wt% of a terpolymer X, wherein X is a reactive functional comonomer. For example, X can be glycidyl methacrylate, maleic anhydride, or a half-ester of maleic anhydride and/or derivatives thereof.
30 Preferably, the terpolymer includes from about 1 wt% to about 4.5 wt% of X, more preferably from about 1.5 wt%

to about 4 wt% of X. Most preferably the terpolymer comprises from about 2 wt% to about 4 wt% of X.

In still another embodiment, the present invention is a terpolymer comprising, in addition to the ethylene and fluoroalkyl comonomers described hereinabove, from about 0.5 wt% to about 50 wt% of a terpolymer Y, wherein Y is a vinyl acetate or an acrylate comonomer, such as methyl acrylate and butyl acrylate. Preferably Y is included in an amount of from about 2 wt% to about 45 wt%, and more preferably from about 5 wt% to about 40 wt%. Most preferably, Y is included in an amount of from about 5 wt% to about 35 wt%. Preferably Y is a vinyl acetate monomer.

In another embodiment, the present invention is a terpolymer comprising, in addition to the ethylene and fluoroalkyl comonomers described hereinabove, from about 1.0 to about 20 wt% of a terpolymer Z, wherein Z is acrylic acid or methacrylic acid comonomer. Preferably Z is included in an amount of from about 1.5 wt% to about 18 wt%, and more preferably from about 2.5 wt% to about 17 wt%. Most preferably Z is included in an amount of from about 3 wt% to about 15 wt%.

In still another embodiment, the present invention is a fluorine-containing ethylene copolymer comprising, in addition to at least 40 wt% ethylene and from 0.5 wt% to about 40 wt% fluoroalkyl comonomer, any combination of at least two comonomers selected from the group consisting of X, Y, and Z in a total amount of from about 0.5 wt% to about 59.5 wt%. Preferably the two comonomers are present in a total amount of from about 2 wt% to about 50 wt%, more preferably in an

amount of from about 5 wt% to about 45 wt%, and most preferably in an amount of from about 7 wt% to about 40 wt%. Preferably the combination includes Y.

In another embodiment, the present invention is a
5 composite film that includes at least one layer of an ethylene/fluoroalkyl copolymer of the present invention. A composite film of the present invention can be obtained in the same manner as composite films comprising conventional polyethylene polymer or
10 copolymer layers with other polymer layers. For example, U. S. Pat. No. 3,589,976 describes a process suitable for making the composite films of polystyrene polyolefins made by a coextrusion process. Composite films of the present invention can include laminate
15 composite films, with or without adhesive layers.

In another embodiment, the present invention is a composite fiber that includes at least one component of an ethylene/fluoroalkyl copolymer of the present invention. A composite fiber of the present invention
20 can be obtained in the same manner as composite fibers comprising conventional polymers. U.S. Pat. No. 3,329,557 describes a preparation of composite fibers of nylon and poly(ethylene terephthalate) for making antistatic filaments.

25 Copolymers of the present invention can be used alone or in blends with other polymers, for example, thermoplastic materials and thermoplastic elastomers. Polymers suitable for blending with copolymers of the present invention include, for example: polyamides,
30 polyethylene terephthalate, polyurethane, polystyrene, polyethylene, ethylene copolymers, and polypropylene. Blends of the present invention include from about 1

wt% to about 99 wt% of the fluorine containing ethylene copolymer of the present invention. Preferably blends of the present invention comprise from about 5 wt% to about 95 wt% of the fluorine-containing ethylene
5 copolymer, more preferably from about 10 wt% to about 90 wt% , and most preferably from about 20 wt% to about 80 wt%.

In another embodiment, the present invention is a release resin useful for making low surface energy
10 release films. The copolymers of the present invention can be converted into a film layer that has good release from adhesives, for example. A copolymer of the present invention can be co-extruded with low-density polyethylene to form an outer pouch for
15 packaging merchandise. Alternatively, the resin can be co-extrusion coated onto paper to form a release backing for tapes and labels.

In another embodiment, the present invention is a melt-blown fiber comprising a fluorine-containing
20 ethylene copolymer (FCEC) as described herein. For example, a FCEC or a FCEC polymer blend can be made into melt-blown fibers possessing high water repellency, and can be useful for medical and hygiene applications. A FCEC can be blended with polyethylene
25 or polypropylene, for example. Polyolefin-based melt-blown non-woven materials can require a coating of fluorochemical for water and oil repellency. The coating process can involve using an organic solvent for the fluorochemical, a heat treatment step and a
30 curing step to adhere the fluorochemical to the non-woven surface. This process can be of concern for

environmental reasons, and also may adversely affect the delicate polyolefin fibers.

In another embodiment, the present invention is a composite or multilayer structure having an outer layer comprising a FCEC. A composite structure of the present invention can be used in applications that require periodic cleaning of the surface of the composite structure, such as on cooking utensils, or on the heated surface of an iron, for example. Composites of the present invention can be used in packaging applications to provide an easy cleaning, water repellent, oil repellent, non-staining low friction package surface, or in cladding applications - particularly architectural cladding - to provide the same type of surface.

In still another embodiment, the present invention is a microporous membrane obtained from a FCEC described herein. A microporous membrane of the present invention can be prepared, for example, by drawing particulate-laden FCEC films or particulate-laden films of FCEC/polymer blends. The drawing process causes said film to separate from the particulate thereby creating microvoids which are small enough to prevent liquid water transport but large enough to allow water vapor transport through the film. The low surface energy microvoids created when using FCEC or FCEC/polymer blends have superior resistance to liquid (e.g. water, organic, blood) penetration making them suitable for use in performance outerwear, protective apparel, operating room apparel and furnishings, and a variety of home and construction applications such as

housewrap, roof liners, and undercarpet spill barriers, for example.

In still another embodiment, the present invention is a flash spun plexifilamentary nonwoven or yarn product comprising a FCEC or FCEC/polymer blend. Consolidated webs of plexifilaments have superior liquid penetration resistance due to the low surface energy inherent in fluorine-enriched surfaces making superior "housewrap" and protective apparel candidates. Applications include housewrap, roof liners, and undercarpet spill barriers, for example.

In still another embodiment, the present invention is a melt spun fibrous product, for example fibers, spun yarns, spunbonded nonwovens, obtained from blends of FCEC and/or by multicomponent fiber spinning (e.g., sheath-core) to enhance the surface properties by fluorine enrichment. FCEC and blends thereof can further be used as carriers for color concentrates which, when blended with other olefins prior to melt spinning, yield not only producer-colored but also fluorine-enriched low surface area fibers. Melt spun fibers from polymers of this invention have reduced coefficient of friction. Fabrics therefrom have reduced:

- tendency to chafe or abrade skin, reducing irritation and blister formation (e.g., athletic socks),
- wind resistance, improving sport performance (e.g., speed sports apparel for bicycling, skating, skiing)
- surface stickiness, improving filtration performance (e.g., reduced backpressure, enhanced dust cake release).

Fibers and fabrics including nonwoven fabrics of these polymers exhibit improved stain resistance. Reduced surface reactivity makes these materials more suitable for biomedical applications (e.g., sutures, vascular grafts, patches) than standard polyolefins.

40

EXAMPLES

The following examples are merely illustrations of the present invention, and not intended to limit the scope of the present invention in any way.

5 Testing

Melt Index (MI) was measured using ASTM D1238 using a 2160 gram weight, and measured at 190°C. Melting Point was measured using Differential Scanning Calorimetry (DSC), using a DuPont Thermal analyzer.

10

Surface tension (surface energy) was measured on blown films of the Examples and the Comparison Examples using a Video Contact Angle System instrument, for AST PRODUCT, Inc. The film samples of 3-4 mil were made
15 from a laboratory blown film equipment. Surface tension was calculated base on the Harmonic-Mean Method as described in Polymer Interface and Adhesion, Sougeng Wu, Marcel Dekker, Inc., 1982. Deionized water having a surface tension of 71.8 dynes/cm and methylene iodide
20 having a surface tension of 50.8 dynes/cm were used in the contact angle measurements.

Analysis of fluorine content was by Ion Chromatography (IC). The samples were combusted in oxygen-filled sealed flasks. The combustion gases were
25 collected in a weakly basic catch solution. The catch solution was taken to a known volume and analyzed by IC.

Compositions of ethylene/perfluoroalkyl (meth)acrylate copolymers were measured and calculated
30 by fluorine content alone. Compositions that include vinyl acetate and methyl acrylate were measured by a

combination of fluorine content analysis and infrared spectroscopy (IR).

Ethylene copolymers listed in Table 1 were prepared according to the following procedures.

5 Ethylene was copolymerized in the presence of fluoroalkyl(meth)acrylate monomers. The free radical polymerizations were carried out at high pressure (27,000 psi) and a temperatures ranging from 160°C to 250°C, in the presence of a peroxide free radical
10 initiator.

Example C1 is not an example of the present invention, and is a copolymer of ethylene and methacrylic acid, prepared under the same conditions as the examples of the present invention.

15 Example 1 is a terpolymer of ethylene, methacrylic acid, and Zonyl® TA-N

Examples 2-6, Example 9 and Examples 11-19 are copolymers of ethylene and either Zonyl® TA-N or Zonyl® TM.

20 Examples 7 and 8 are terpolymers of ethylene, vinyl acetate, and Zonyl® TM.

Example 10 is a terpolymer of ethylene, methyl acrylate and Zonyl® TM. It is an amorphous polymer without a melting point.

25 The blends of fluorine-containing copolymers, Examples 20-26, are listed in Table 2. The blends were prepared in a 30 mm twin screw extruder.

Example C2 is not an example of this invention, and is a low density polyethylene with a MI of 4.4 and
30 a melting point of 115 °C.

Examples 20-21 and Examples 23-24 are blends of LDPE described in C2, and either Zonyl® TM or Zonyl® TA-N.

Example 22 is a blend of PP and Zonyl® TM. The PP is a polypropylene with a MI of 1.5 and a melting point of 166 °C.

Examples 25-26 are blends of HDPE and Zonyl® TA-N. The HDPE is a high-density polyethylene with a MI of 0.6 and a melting point of 139 °C.

Zonyl® TA-N and Zonyl® TM are both available from E.I. DuPont de Nemours and Company. Zonyl® TA-N is a perfluoroalkylethyl acrylate of the general formula: $C_nF_{2n+1}CH_2CH_2O(CO)CH=CH_2$, wherein n is an integer from 5 to about 20. Zonyl® TM is a perfluoroalkylethyl methacrylate of the general formula: $C_nF_{2n+1}CH_2CH_2O(CO)C(CH_3)=CH_2$, wherein n is an integer from 3 to about 20.

Table 1
Examples (Ex.) 1 - 19
Copolymers of Ethylene and
Perfluoroalkyl(meth)acrylate

Ex.	Composition (wt%)	F content (wt%)	MI at 190°C	Melting Point (°C)	Surface Tension (dynes/cm)	Polymer ization Temp (°C)
C1	E/MAA (90/10)	0.0093	122	96	34.8	250
1	E/MAA/TAN (89/10/0.6)	0.4	96	96	31.3	250
2	E/TAN (99.4/0.6)	0.38	69	110.4	30.6	250
3	E/TAN (99.2/0.8)	0.52	29	110	28.63	250
4	E/TM (99.5/0.5)	0.3	82	111	30.1	250
5	E/TM (98.9/1.1)	0.63	81	111	29.5	250
6	E/TM (97.6/2.4)	1.45	123	110	25.2	250
7	E/VA/TM (71.9/24.5/3.6)	1.98	43	72	26.2	210
8	E/VA/TM (80/17.2/2.8)	1.48	37	87	29	210
9	E/TM (93.3/6.7)	4.0	144	109	23.1	260
10	E/MA/TM (34/62/3)	1.78	14	Amorphous	NA	165
11	E/TM (93.8/6.2)	3.69	22	117.6	23	210
12	E/TM (91.9/8.1)	4.84	28	117.2	22	210
13	E/TM (93.3/6.7)	4	14	118.3	24.5	190
14	E/TM (93.7/6.3)	3.76	20	114	24.6	230
15	E/TM (93.5/6.5)	3.9	35	112	24.2	250
16	E/TAN (93.4/6.6)	4.2	16	114.3	24.6	210
17	E/TAN (92.9/7.1)	4.5	52	114	25	210
18	E/TAN (88.4/11.6)	7.4	80	112.7	22.3	210
19	E/TAN (84.7/15.3)	9.7	110	110	21	210

5 E = ethylene; TAN = Zonyl® TA-N; TM = Zonyl® TM; MAA = methacrylic acid; VA = vinyl acetate
MA: methyl acrylate; F = fluorine.

Table 2. Surface Properties of Blends of
Ethylene/Perfluoroalkyl(meth)acrylate Copolymers

<u>Examples</u>	<u>Blend Composition (wt.%)</u>	<u>Surface Tension (dyne/cm)</u>
C2	LDPE	33.6
20	LDPE/Example 9 (80/20)	25.5
21	LDPE/Example 9 (60/40)	24.2
22	PP/Example 9 (80/20)	27.0
23	LDPE/Example 12 (60/40)	24.1
24	LDPE/Example 13 (60/40)	23.7
25	HDPE/Example 12 (60/40)	26.2
26	HDPE/Example 13 (60/40)	24.7

CLAIMS:

1. A film comprising a fluorine containing ethylene copolymer (FCEC) obtained by the copolymerization of ethylene with suitable fluorine-containing comonomer compounds, wherein the FCEC comprises from about 0.5 wt% to about 40 wt% of a fluorine-containing comonomer compound and from about 30 wt% to about 99.5 wt% ethylene.
2. A fiber comprising a fluorine containing ethylene copolymer (FCEC) obtained by the copolymerization of ethylene with suitable fluorine-containing comonomer compounds, wherein the FCEC comprises from about 0.5 wt% to about 40 wt% of a fluorine-containing comonomer compound and from about 30 wt% to about 99.5 wt% ethylene wherein the fiber is obtained by a melt-blowing process.
3. An article having a composite or multilayer structure comprising an outer layer comprising: a fluorine containing ethylene copolymer (FCEC) obtained by the copolymerization of ethylene with suitable fluorine-containing comonomer compounds, wherein the FCEC comprises from about 0.5 wt% to about 40 wt% of a fluorine-containing comonomer compound and from about 30 wt% to about 99.5 wt% ethylene.
4. A microporous membrane comprising a fluorine containing ethylene copolymer (FCEC) obtained by the copolymerization of ethylene with suitable fluorine-containing comonomer compounds, wherein the FCEC comprises from about 0.5 wt% to about 40 wt% of a

fluorine-containing comonomer compound and from about 30 wt% to about 99.5 wt% ethylene, wherein the membrane is useful as protection against permeation of liquids through the membrane.

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5. A flash spun plexifilamentary product comprising a fluorine containing ethylene copolymer (FCEC) obtained by the copolymerization of ethylene with suitable fluorine-containing comonomer compounds, wherein the FCEC comprises from about 0.5 wt% to about 40 wt% of a fluorine-containing comonomer compound and from about 30 wt% to about 99.5 wt% ethylene.

6. A melt spun fibrous article comprising a fluorine containing ethylene copolymer (FCEC) obtained by the copolymerization of ethylene with suitable fluorine-containing comonomer compounds, wherein the FCEC comprises from about 0.5 wt% to about 40 wt% of a fluorine-containing comonomer compound and from about 30 wt% to about 99.5 wt% ethylene, wherein the fibrous products are obtained by melt spinning or multicomponent fiber spinning a FCEC or a blend thereof.

INTERNATIONAL SEARCH REPORT

Internat Application No

PCT/US 03/07026

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08F210/02 C08J5/18 D01F6/32 D01D5/11

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08F D01F D01D C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 398 250 A (DAIKIN IND LTD) 22 November 1990 (1990-11-22) page 4, line 52	4
X	WO 01 14620 A (SIEMIONKO ROGER K ;DU PONT (US); SHIN HYUNKOOK (US); KRESPAN CARL) 1 March 2001 (2001-03-01) examples 13-16	2,5,6
X	US 5 582 918 A (GOUARDERES RENE) 10 December 1996 (1996-12-10) examples 1-26	1,3
X	US 4 778 866 A (ISAKA TSUTOMU ET AL) 18 October 1988 (1988-10-18) example 5	1,3
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

G document member of the same patent family

Date of the actual completion of the international search

11 September 2003

Date of mailing of the international search report

18/09/2003

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Schmidt, H

INTERNATIONAL SEARCH REPORT

Intern: Application No
PCT/US 03/07026

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	<p>WO 02 072648 A (DU PONT ;CHOU RICHARD T (US)) 19 September 2002 (2002-09-19)</p> <p>page 11, line 23</p> <p>page 10, line 4</p> <p>page 10, line 16</p> <p>-----</p>	1-3,5,6

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Interr I Application No

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